Plasma Copolymerization of Ethylene Glycol and Allylamine

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Summary: This work presents the plasma copolymerization of Ethylenglycol and Allylamine with the purpose to obtain thin films of biocompatible random polymers with N—H and O—H chemical groups. The synthesis used electrical glow discharges with mixtures of the monomers at 13.56 MHz, 10^{-1} mbar and power between 40 and 120 W. The results were thin films of copolymers with N—H, C—H, O—H, and C=C groups of the monomers. The main thermal degradation of the plasma copolymers was found between 100 and 500 °C in one step, suggesting that the material behaves as only one chemical species and not as a mixture. The copolymers absorb an average of 6% of water. The contact angles between the polymers and drops of solutions with concentrations of salts similar to those in the human body vary from 20° to 52° increasing with the power of synthesis. The surfaces varied from smooth to rough as the power of synthesis increases. This physical effect appears as the main variable in increasing the contact angles in the plasma copolymers. The electrical conductivity was in the interval of 10^{-8} and 10^{-13} S/m and was considerably influenced by the water content in the polymers. All these data suggests that the plasma copolymers are partially hydrophilic and biocompatible.

Keywords: allylamine; biocompatibility; ethylenglycol; plasma; polymerization

Introduction

The synthesis of polymers by plasma can be studied as a technique for obtaining biocompatible and biofunctional surfaces. This technique is important because different monomers or chemicals can be combined to produce new materials with the main properties of the components. The plasma techniques have an additional advantage, ramifications and/or crosslinking can be handled for specific applications.[1,2]

Polyethylenglycol (PEG) and polyallylamine (PAl) are biocompatible materials because they have OH and NH groups in their structure that can join with some chemical groups in the living tissues. PEG has been used in materials for implants, biosensors, administration of medicine systems, etc; and combined with polypyrrole, it has been also used in the reconnection of neuronal cells in the spinal cord with promising results.[1–5] On the other hand, PAl has been used in biological applications to promote the adhesion and growth of cells, which increase the biocompatibility of different materials.[6–8] Considering these characteristics, a copolymer formed with both components can be a biocompatible material to be used in the reconnection of neuronal system after a severe lesion. This

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work studies the synthesis of this kind of copolymer.

Experimental Part

Synthesis

Ethylenglycol (Tecsiquim, 99.5%) and allylamine (Aldrich, 95%) (PEG/PAl) were polymerized by plasma in a tubular glass reactor with diameter and length of 9 and 26 cm, respectively. The reactor has stainless steel flanges at the ends with three accesses. In the central ports, stainless steel electrodes were introduced with a separation of 6 cm between them. The electrodes are 21.5 cm long with diameter of 7 cm connected to a RFX-600 Advanced Energy radio frequency generator. In the other accesses, an Alcatel Pascal 2015C1 vacuum pump and a liquid-nitrogen Alcatel LNT 25S condenser for residual gases were connected.

The monomers were placed in different containers connected to the reactor using different access. The ethylenglycol was heated up to 60 C to vaporize. The allylamine vaporized at room temperature with the low pressure in the reactor. Both vapors were continuously fed to the reactor and mixed inside. The plasma was produced with the mixtures without other carrier gases inducing electric glow discharges between the electrodes in resistive mode at 13.56 MHz, 10^{-1} mbar and power in the range of 40 to 120 W.[9] The time of polimerization was 240 minutes. The PEG/PAl copolymers were obtained as thin films adhered to the inner surfaces of the reactor. After the synthesis, the films were washed and swelled with acetone and hot water and later separated from the walls with a thin spatula.

Characterization

The IR analysis of the copolymers was realized with a Perkin-Elmer FT-IR 2000 spectrophotometer applying 32 scans to the films without substrates. The thermal scans were taken in a Thermal Analysis Instrument 51 with a heating ramp of 10 C/min in a Nitrogen atmosphere. The average thickness of the films was calculated measuring in 10 different points with a Mitutoyo micrometer. The electric conductivity of the polymers was calculated obtaining the resistance of the films with a Hewlett-Packard 4329A high resistance meter between two copper electrodes. The voltage applied was between 10 and 250 V at temperatures between 20 and 100 C. The temperature was obtained with a Mastech Mas-345 Digital Multimeter. The micrographs were taken with a Jeol JSM-5900LV scanning electron microscope. The contact angles were obtained taking photographs of the drop-surface systems with a Sony Cyber Shot DSC-S30 camera, 1.6 Megapixels, processed with the DropSnake 2.0 program to calculate the angles.

Results and Discussion

Thickness of PEG/PAl Films

Thermodynamic conditions like pressure and energy applied to synthesis influence the growth of the polymers as thin films. Variations in these conditions result in the formation of consecutive layers with different thickness. The plot in Figure 1 has the total average thickness of PEG/PAl films as a function of the power of synthesis. The tendency is linear, increasing proportionally with the power, from 5.7 to 21 μm, with a growth rate of 191 nm/W.

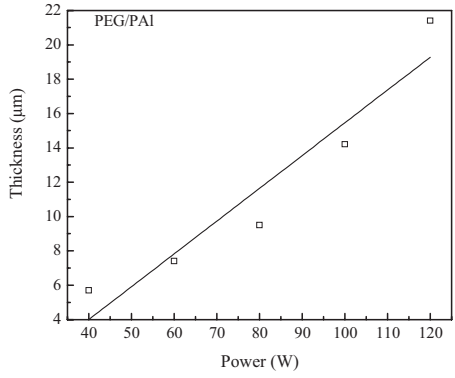

Figure 1.
Thickness of PEG/PAl films.

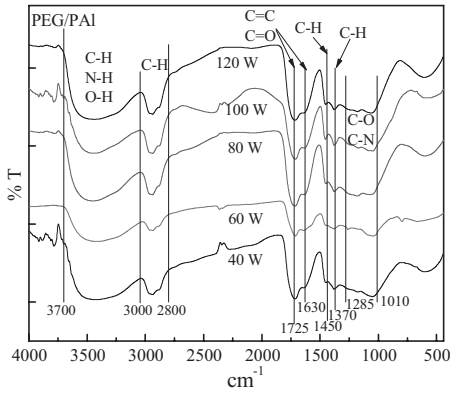

Figure 2.
IR Spectra of PEG/PAl.

FT-IR Analysis

The spectra of Figure 2 contain the IR absorption of PEG/PAl films synthesized at a different power, from 40 W to 120 W, to study the evolution of the main O–H and N–H groups in the polymers. The results show wide and complex absorptions in all IR regions. In the intervals located at 3000-2800 and 1450-1370 cm^{-1}, the absorption of saturated –C–H groups can be found. Both monomers have these groups. In 1725 and 1630 cm^{-1} the signals of unsaturated C=C and C=O groups are present. It is important to remark that these groups have a significant presence in the copolymers. The C=C bonds come from the allylamine portion.

The C=O groups may arise from the ethylenglycol fraction unsaturated during the plasma polymerization, because this compound has only single-bond oxygenated –C–O–H groups. Another source of oxidation in plasma polymers is the neutralization of the last radicals produced during the polymerization with the atmospheric oxygen at the end of the chemical reactions.

The =C–H, N–H and O–H groups can be located between 3700 and 3000 cm^{-1}. They come from the monomers, but the wide absorption also indicates water content in the polymers. Hydrophilicity is very important in biocompatible polymers. The region between 1285 and 1010 cm^{-1} has C–O and C–N vibrations. Thus, all the main chemical groups of ethylenglycol and allylamine are found in PEG/PAl plasma copolymers.

Thermal Analysis

The thermal degradation of PEG/PAl synthesized at different power is shown in Figure 3(a) and 3(b). The thermograms shows water content between 4% and 8% and two intervals of degradation. The first one is located between 100 and 500 °C, centered at approximately 400 °C, and belongs to the main decomposition of the polymers. It is important to highlight that this decomposition occurs in one step, which suggest that the plasma copolymers behave as only one chemical species and not as a mixture of polymers. However, the differences in the decomposition suggest polymers with different molecular weight. The second degradation follows a monotonic

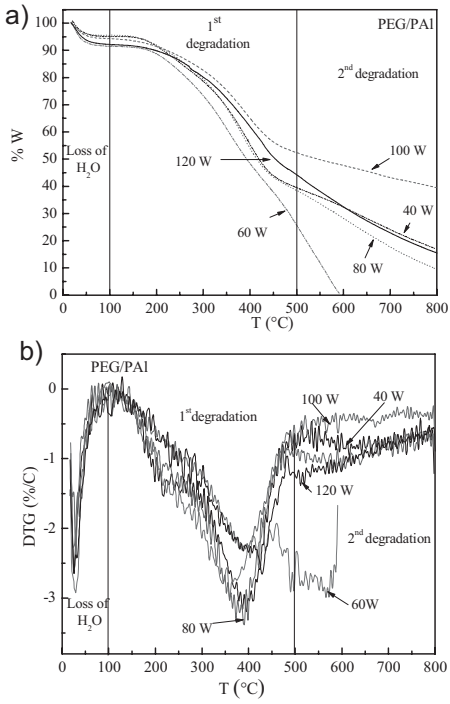

Figure 3.
Thermal degradation of PEG/PAl (a) Thermogravimetric and (b) Differential Thermogravimetric Analysis.

behavior up to 800 C, where the residual mass varies between 0 and approximately 40%. This decomposition can be attributed to the final decay of the remnants.

Electrical Conductivity of PEG/PAl

The electrical conductivity is strongly influenced by the interaction of the polymers with other factors as humidity or solvents. Figure 4 shows the electrical conductivity of PEG/PAl as a function of temperature, from 20 C to 100 C. The polymers were heated and the conductivity measured in two steps, during the increase and the decrease of temperature. During the increase, the water in the polymers is evaporating and the conductivity shows this effect with disperse values. However, during the decrease of temperature, after the humidity or solvents are evaporated, the intrinsic conductivity of the materials can be obtained. Sometimes, several cycles of heating-cooling are needed in order to evaporate most of the humidity or solvents in the polymers. In this work, only one increase and decrease was applied. The temperature did not exceed 100 C, because the thermal analysis showed that at this point, the first degradation of the polymers begins.

Figure 4(a) shows the conductivity during the heating. It can be noted that the conductivity shows a continuous increase reaching up to three orders of magnitude, from 10^{-12} to 10^{-8} S/m, from 20 C to approximately 60 C. After that, the samples show dispersed values, which can be a consequence of the loss of water in the polymers. Figure 4(b) shows the conductivity during the cooling step. The tendency is an almost uniform decrease up to three orders of magnitude, from 10^{-10} to 10^{-13} S/m. If we consider that this step is less influenced by the interaction with water or other residual solvents, these values show an approximation to the intrinsic electric conductivity of the polymers. This conductivity indicates that the plasma copolymers are in the insulating regime. However, the water content found in the polymers (4%–8%), increases the conductivity in approximately one order of magnitude.

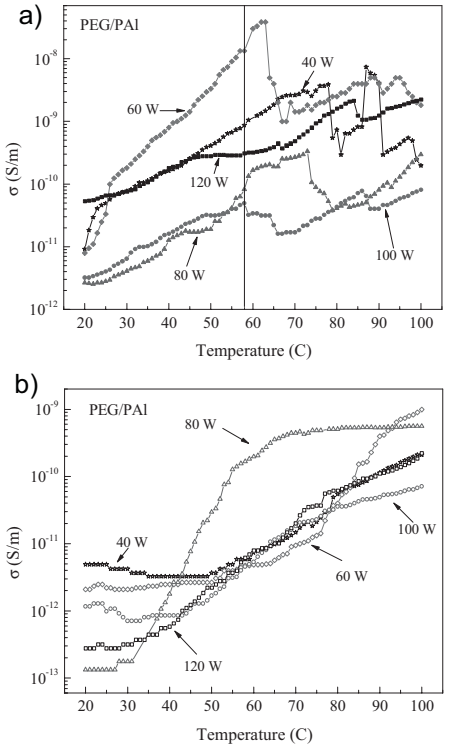

Figure 4.
Electrical Conductivity of PEG/PAl during the (a) heating and (b) cooling steps.

Contact Angle of PEG/PAl with Different Ionic Solutions

The contact angle of surfaces with drops of solutions is function of physical and chemical variables, among others, morphology, energy of surfaces and chemical nature of solutions. The contact angles represent a correlation between cohesive and dispersive forces at the interface. If the dispersive forces dominate, the wet area increases, the contact angles have low values and the surface tends to be hydrophilic. On the other hand, if the wet area is small, the contact angles are high and the material tends to be hydrophobic.

In this work, the contact angles of PEG/PAl plasma copolymers were studied with

drops of water and solutions of NaCl (118 mM) and a Krebs-Ringer (KB) composition (NaCl 118 mM, KH_2PO_4 1.3 mM, KCl 4.7 mM, $CaCl_2$ 2.5 mM, $MgSO_4$ 1.17 mM, $NHCO_3$ 25 mM). The concentrations of salts in the solutions are similar to those in the extra-cellular fluids of the human systems.

The contact angles of the solutions in the plasma copolymers as a function of the power of synthesis are shown in Figure 5. The values vary from 20° to 52° increasing with the power of synthesis of PEG/PAl. This variable can be reflected in the physical characteristics of the polymeric surfaces. The NaCl solution has an almost linear increase; however, the water and KB solution have dispersed values at low power of synthesis. On the contrary, polymers synthesized at 80 W and 100 W have very similar contact angles for all the solutions.

The values suggest that the polymers are hydrophilic and that the chemical affinity between fluids and the characteristics of the surfaces are more important in low-power synthesis polymers. PEG/PAl at 40 W and water has the lowest contact angles, 20°, but on the other hand, the copolymer at 100 W and water has the highest angles, 52°.

Morphology of PEG/PAl.

Figure 6 shows micrographs of PEG/PAl synthesized at different power to see the influence of this variable in the morphology of the polymers. At 60 W, the polymers are formed with several consecutive thin compact layers, see Figure 6(a). The individual layers have thicknesses between 1 μm and 2 μm approximately. This is not the total thickness discussed in section 3.1. Between the layers, there are empty spaces that produce spongy polymers. Fluctuations in the variables of synthesis could be the cause of this layered morphology.

In Figure 6(b), the micrograph of the copolymer synthesized at 60 W shows a compact layer with a smooth surface. As the power increases, the roughness also increases in the polymers, see Figure 6(c) and 6(d). This physical effect appears as the main variable in increasing the contact angles in the plasma polymers.

Random plasma copolymers synthesized with pyrrole and ethylene glycol resulted in much more roughed surfaces and porous layers which produced lower contact angles, between 11° and 18°, with the same solutions of this work. In those copolymers, the contact angles decreased with the power of synthesis.[10] This opposite effect, compared with the results of this work, could be attributed to the porous in the body of the pyrrole/ethylene copolymers.

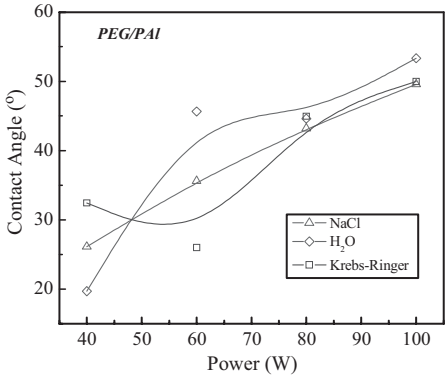

Figure 5.
Contact angle PEG/PAl.

Conclusions

Ehtylenglycol and allylamine were randomly combined in electric glow discharges to synthesize by plasma thin layers of copolymers with the main chemical groups of both components. The results indicated that the films have the OH and NH groups of the monomers and that they decompose thermally as one chemical species, not as a mixture of polymers. The copolymers absorb an average of 6% of water indicating that they are hydrophilic. This is mandatory in biocompatible materials.

Another important variable in the hydrophilicity of the polymers is the contact angles between the surfaces and drops of solutions with concentrations of salts similar to those in the human body. The values vary from 20° to 52° increasing with the

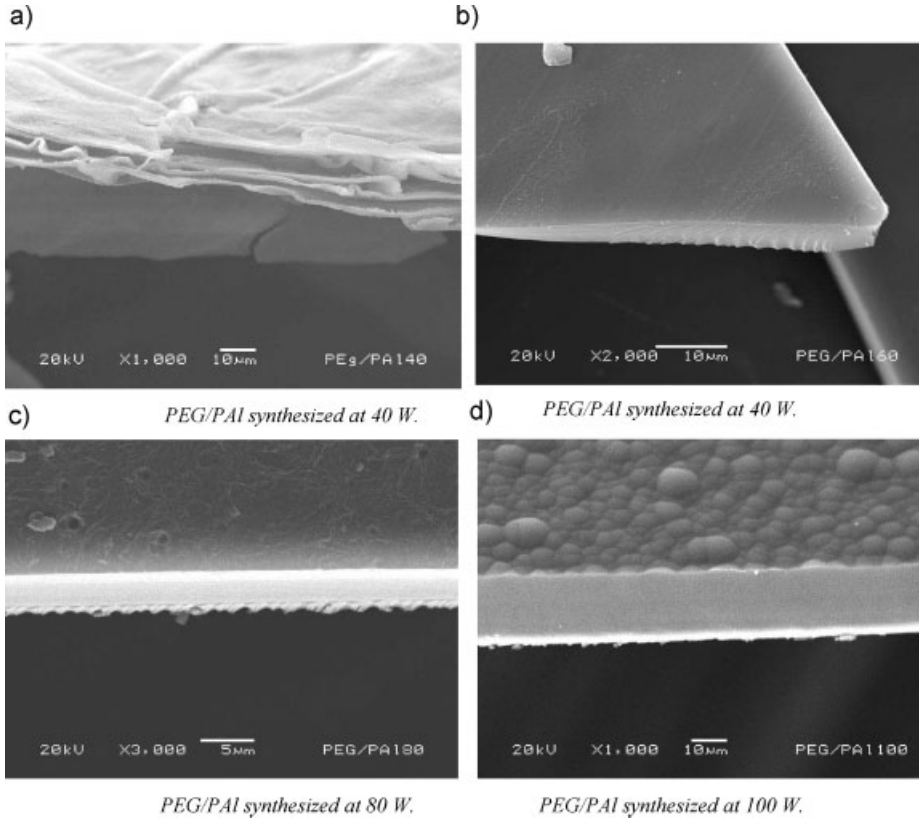

Figure 6.
Morphology of plasma copolymers of ethylenglycol and allylamine at different power of synthesis.

power of synthesis of PEG/PAl. The morphology of surfaces varied from smooth to roughed surfaces as the power of synthesis increases. This physical effect appears as the main variable in increasing the contact angles in the plasma copolymers.

The electrical conductivity was between 10^{-13} and 10^{-8} S/m, and is different during heating and cooling processes. This behavior can be associated to the humidity absorbed in the polymers, which modify the conductivities in approximately one order of magnitude.

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